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Opportunities for Electrochemical Capacitors as Energy-Storage Solutions in Present and Future Navy and Marine Corps Missions

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14. ABSTRACT

Electrochemical capacitors (ECs) are an emerging class of energy-storage devices whose performance metrics span the critical gap that presently exists between the high power density derived from electrostatic capacitors and the high energy density of batteries. Because of their distinctive operational characteristics, there is growing interest in developing and deploying EC technologies for civilian and military applications, ranging from microelectronics to hybrid–electric generation systems to backup power, all of which have challenging energy/power requirements. This report first summarizes the types of EC technologies that are commercially available, and describes their general performance characteristics and common uses. Next, the author will identify specific Navy/Marine Corps applications where EC-based energy storage will be an enabling technology for critical missions, drawing from present research and development efforts within the Navy and other Department of Defense agencies, and extrapolating from related uses in the private sector. Finally, the continued evolution of EC technologies is discussed in the context of extending their utility for future civilian and military applications.

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INTRODUCTION AND BACKGROUND

Electrochemical capacitors[1] are a class of energy-storage devices that exhibit characteristics related to both electrostatic capacitors and conventional batteries.[2,3,4,5] In terms of both design and function, ECs are most closely related to batteries in that both are based on electrochemical cells that typically incorporate liquid or gel electrolytes, which ultimately limits their operational voltages to <5 V, in contrast to solid-state electrostatic capacitors that can be charged to kV levels, limited only by the breakdown strength of the incorporated dielectric material (typically a polymer or ceramic). Despite their significantly lower single-cell voltages, ECs and batteries exhibit a clear advantage in terms of energy density (see Figure 1), owing to the superior charge-storage capacities of electrochemical mechanisms, as compared to the energy stored in the electric field imposed across the dielectric material in an electrostatic capacitor. However, in the case of electrochemical charge-storage the required transport of solvent, ions, and electrons—and the lower mobility of molecules and ions relative to electrons—limits the power characteristics of ECs and batteries with respect to electrostatic capacitors.

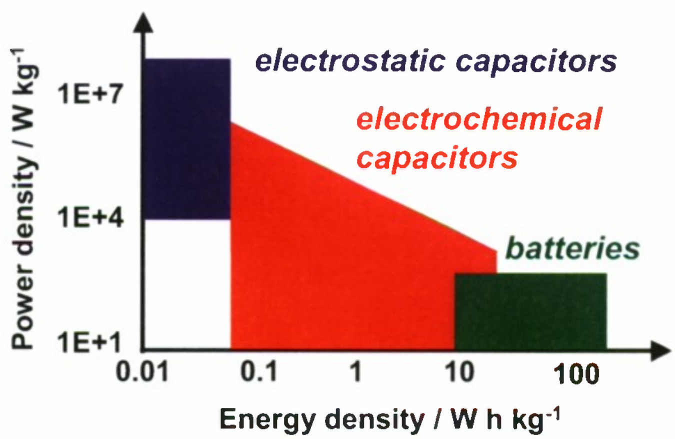

Figure 1. Diagram of approximate power and energy density ranges of current battery and capacitor energy-storage technologies.

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1. Electrochemical capacitors are often denoted as "supercapacitors" or "ultracapacitors".
2. B. E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Kluwer Academic/Plenum Publishers, New York (1999).
3. B. E. Conway, "Transition from 'Supercapacitor' to 'Battery' Behavior in Electrochemical Energy Storage," *J. Electrochem. Soc.* **138**, 1539 (1991).
4. A. Burke, "Ultracapacitors: Why, How, and Where is the Technology," *J. Power Sources* **91**, 37 (2000).
5. R. A. Huggins, "Supercapacitors and Electrochemical Pulse Sources," *Solid State Ionics* **134**, 179 (2000).

Manuscript approved September 26, 2009.

Electrochemical capacitors are commonly differentiated from batteries in that at least one of two electrodes in an EC relies on double-layer capacitance at the electrode/electrolyte interface as the principal charge-storage mechanism. As a result, ECs typically exhibit sloping charge–discharge profiles that are reminiscent of electrostatic capacitors (thus their designation as "electrochemical capacitors"). Due to the combination of sloping charge–discharge profiles and the lower charge-storage capacity of the double-layer mechanism relative to the redox processes in batteries, ECs exhibit lower energy densities than batteries. For example, the energy density of a typical carbon–carbon EC is 3 – 5 $W\,h\,kg^{-1}$ as compared to >100 $W\,h\,kg^{-1}$ for high-performance Li-ion batteries. Compared to advanced batteries, the chief advantages of ECs are the rates at which their energy can be stored and released (charge–discharge response times are typically <10 seconds for carbon–carbon ECs), long cycle life (often hundreds of thousands of cycles), and graceful fade characteristics. The sloping charge–discharge profiles of ECs also provide an important benefit as an indicator of the state-of-charge of EC cells as they are electrochemically cycled.

The term "electrochemical capacitor" is used to describe a diverse array of energy-storage devices that incorporate a variety of active materials (high-surface-area carbons, electroactive polymers, and/or transition metal oxides), electrolytes (conventional aqueous and nonaqueous electrolytes, advanced polymer electrolytes, or ionic liquids), cell configurations (symmetric and asymmetric), and electrode architectures. Because of this diversity in design and cell chemistry, as a class of energy-storage technologies, ECs cover a broad region on the power *vs.* energy density plane, and bridge the critical performance gap that exists between the high power densities offered by conventional capacitors and the high energy densities of batteries, as shown in Figure 1. With the continued evolution of new

technologies and applications that have challenging power requirements, ECs are now being considered as viable energy-storage solutions, either as stand-alone devices for high-power needs or more often as integral components in hybrid systems that also include other energy storage/generation technologies (*e.g.*, batteries, fuel cells, combustion engines).[6]

The fast charge–discharge characteristics and long cycle life of ECs are particularly well suited for hybrid–electric power systems that are designed to recapture energy from repetitive motion that would normally be wasted by conventional braking. The most visible applications of hybrid–electric systems are for transportation, with examples ranging from compact cars to garbage trucks and city buses. The same concepts of energy recapture are also being applied to many industrial platforms, including fork-lifts, cranes, and elevators. In all such cases, hybrid–electric systems, as enabled by energy storage with ECs, can provide significant energy/fuel savings and reduction in harmful emissions. Electrochemical capacitors are also being deployed in many other roles including as high-power backup energy storage for portable and stationary applications, and for various load-leveling and peak-shaving duties for applications in industrial and utility sectors.

The development and commercialization of electrochemical capacitor technology is still in its infancy compared to battery technology, but the demonstrated capabilities of even current EC technology is sufficient to warrant increasing interest from a variety of sectors. The future evolution of EC technology is being driven by continuing basic and applied research efforts in laboratories worldwide, with particular emphasis on advances in nanoscience that will result in new high-performance electrode materials and electrolytes, and a

6. J.R. Miller and A.F. Burke, "Electrochemical Capacitors: Challenges and Opportunities for Real-World Applications," *Interface* **17 (1)**, 53 (2008).

more detailed understanding of important fundamental processes at the electrode/electrolyte interface. Next-generation EC technologies based on these new materials and discoveries should demonstrate improved performance in terms of these mission-critical areas: energy density, response time, and cycle life.[7,8]

Objectives

The overarching goal of this report is to identify present and future opportunities where ECs can impact current, and enable future Navy and Marine Corps missions. En route to that goal, the author first summarizes the general performance characteristics of two classes of commercially available ECs, electric double-layer capacitors (EDLCs) and asymmetric aqueous ECs, and also describes some of the commercial sector applications that are currently being explored with each type of EC. Specific companies and products that are referenced in this report are included as examples of the current status of commercially available ECs, and their mention does not imply an endorsement of particular technologies or suppliers.

The author will then identify more specific applications and technologies of relevance to the Navy and Marine Corps. To identify opportunities for EC deployment, the author has collected information from a variety of sources, including the open scientific literature, internet resources, and discussions with relevant program managers and scientists within the Department of Defense. In a few cases, there are specific programs within the Navy or broader DoD where commercial ECs are already being evaluated as power source components, and

7. J.W. Long, "Current Status and Future Research Opportunities for Electrochemical Capcitors: Relevance for Naval and Civilian Applications," NRL Memorandum Report (NRL/MR/6170--08-9119), 14 March 2008.
8. P. Simon and Y. Gogotsi, "Materials for Electrochemical Capacitors," *Nature Mater.* **7**, 845 (2008).

those programs are described first. The author also takes the liberty to identify potential future applications where ECs should be considered as an energy-storage technology, as based on their well-known operation characteristics and by extrapolating from related uses in the private sector.

In the final section, the author briefly examines how continued evolution of present EC technologies and the development of new EC cell chemistries may further advance their utility in military and civilian applications.

Summary of Commercially Available Electrochemical Capacitor Technologies

Electric Double-Layer Capacitors. The most mature and common form of EC is the "electric double-layer capacitor" (EDLC), whose current form was first invented by the Standard Oil Company of Ohio in 1966.[9] The EDLC incorporates a symmetric cell design comprising two high-surface-area carbon electrodes separated by a nonaqueous electrolyte. As the name implies, charge is stored in the electric double-layer that forms at all electrode/electrolyte interfaces (see Figure 2). The energy density of a symmetric EDLC is defined by the equation, $E = \frac{1}{2} C V^2$, where C is the cell-level specific capacitance (a serial combination of the capacitances of the individual electrodes) and V is the operating voltage of the two-electrode cell.[2] In order to maximize the electrode capacitance, high-surface-area carbons such as activated carbon are typically used as the active electrode material, although more exotic forms of carbon such as aerogels and nanotubes are also being explored.[10,11,12,13]

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9. R. A. Righmire, "Electrical Energy Storage Apparatus," U.S. Patent #3,288,641, 29 November 1966.
10. E. Frackowiak and F. Béguin, "Carbon Materials for the Electrochemical Storage of Energy in Capacitors," *Carbon* **39**, 937 (2001).
11. A. G. Pandolfo and A. F. Hollenkamp, "Carbon Properties and Their Role in Supercapacitors," *J. Power Sources* **157**, 11 (2006).

The square dependency of the voltage term is a more critical factor for determining energy density. Thus, most EDLCs use electrolytes based on nonaqueous solvents, such as acetonitrile or organic carbonates, which enable operative voltages of up to ~2.7 V. With the combination of a high-surface-area carbon and a nonaqueous electrolyte, commercial EDLCs with acetonitrile-based electrolytes exhibit energy densities of ~3 $W\,h\,kg^{-1}$, compared to ~1 $W\,h\,kg^{-1}$ for the same symmetric carbon–carbon configuration using an aqueous electrolyte. The thermal characteristics of the nonaqueous electrolytes used in EDLCs also enable their operation over a wide range of temperatures. For example, acetonitrile-based EDLCs are typically recommended for use between about –40 and +65 °C. Ionic liquids are also being investigated for use in EDLCs as a potential alternative to the volatile organic solvents that are currently used for EDLC electrolytes, but the cost of the ionic liquids remains a hindrance to their large-scale application.[14]

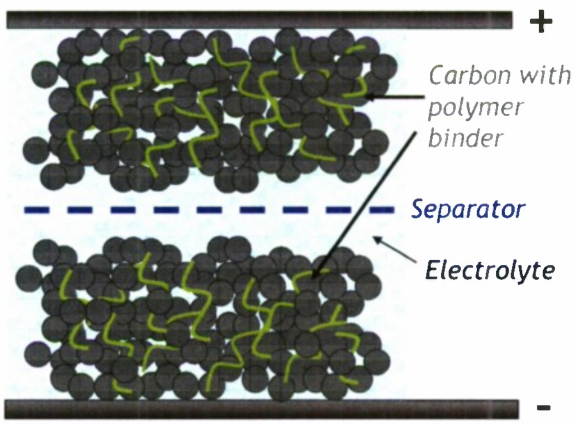

Figure 2. Cross-sectional schematic of a typical EDLC.

The ability to rapidly charge and discharge EDLCs is ultimately derived from the interfacial nature of the double-layer capacitance mechanism, beyond which the nanoscale morphology (pore size distribution, tortuosity, and interconnectivity) of the high-surface-area carbon electrode plays a key role in optimizing the EDLC response time. The microscale electrode and cell architecture is also a key factor in determining the time response of functional

12. E. Frackowiak, "Carbon Materials for Supercapacitor Application," *Phys. Chem. Chem Phys.* **9**, 1774 (2007).
13. P. Simon and A. Burke, "Nanostructured Carbons: Double-Layer Capacitance and More," *Interface* **17(1)**, 38 (2008).
14. See http://www.jrc.co.jp/jp/whatsnew/20061018/index.html.

electrochemical devices, and thus most EDLCs are fabricated with relatively thin (100–200 μm) composite electrode structures made from carbon powder and polymer binder, with opposing electrodes separated by thin porous polymer membranes (typically 25 μm) infused with the liquid or gel electrolyte. On the basis of these factors, commercial EDLCs can be designed to exhibit technology relevant energy densities while achieving charge–discharge response times on the order of one second.

Electric double-layer capacitors are now widely available from such manufacturers/suppliers as Maxwell Technologies, Inc. (San Diego, CA),[15] Nesscap Co. Ltd. (Republic of South Korea),[16] Cooper-Bussman, Inc. (St. Louis, MO),[17] batScap (France),[18] and Cap-XX (Australia). To meet the demands of diverse applications, EDLCs are produced in diverse forms (see Figure 3), ranging from small single-cell 2.7-V capacitors of a few farads to integrated modules of EDLCs that generate voltages (*e.g.*, 125 V) that are more relevant for large-scale applications.

Figure 3. (*a*) a 75-mF, 4.5-V prismatic "supercapacitor" from Cap-XX; (*b*) a 0.22-F, 5.5-V *Powerstor* coin-cell "supercapacitor" from Cooper Bussman; and (*c*) a 125-V "ultracapacitor" module (BMOD0063-P125) from Maxwell.

15. See http://www.maxwell.com/ultracapacitors/index.asp.
16. See http://www.nesscap.com/index.php.
17. See http://www.cooperbussmann.com/.
18. See http://www.batscap.com/en/default.html.

Energy densities for individual EDLC cells range from 3–5 W h kg^{-1} while for integrated high-voltage modules of EDLCs, energy densities are slightly lower (typically 1.5–3.5 W h kg^{-1}). Maximum power densities for cells and modules range from 4 to 26 kW kg^{-1}, depending on the specific cell design. Typical power-discharge profiles are shown in Figure 4 for both a single-cell EDLC (left) and for a 125-V EDLC module (right).[19] Online models and spreadsheets are available to assist in the selection of specific EDLC products for particular power/energy requirements.[20,21,22]

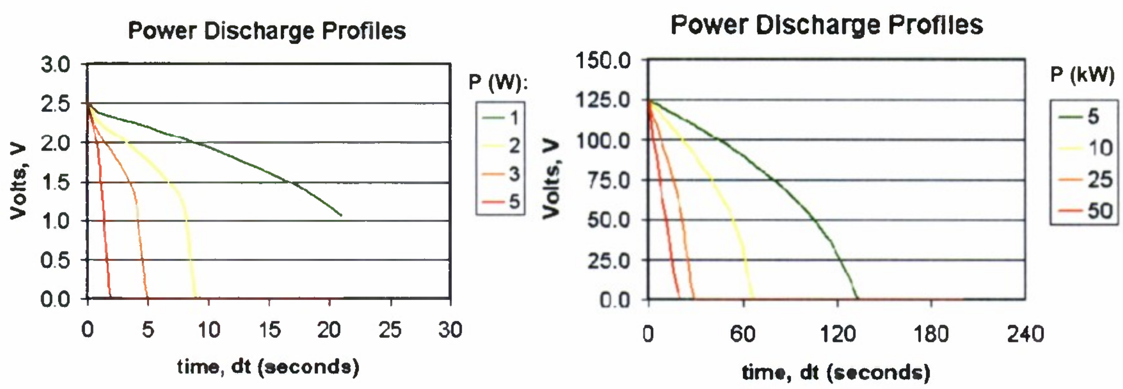

Figure 4. Power–discharge profiles for (left) a 10-F single-cell EDLC (Maxwell model PC-10) and (right) a 125-V EDLC module (Maxwell model BMOD0063-P125).

The EDLCs that are currently on the market have demonstrated cycle lives of hundreds of thousands to more than one million cycles. Although "high-rate" lithium-ion batteries have made great advances recently in terms of power density to become more competitive with EDLCs, the cycle life of even advanced batteries is still typically limited to a few thousand cycles. Although current EDLCs are generally more expensive than conventional batteries, their higher initial cost is often compensated by their long cycle life and associated low maintenance. The

19. See http://www.maxwell.com/files/xls/20080717_power_charts_1.6.xls.
20. See http://www.maxwell.com/ultracapacitors/technical-support/tools-models.asp.
21. See http://www.cooperbussmann.com/otherFiles/eeca4652-2ec7-4a1b-9a19-ffa15e4b8694.xls.
22. See http://www.cap-xx.com/resources/designaids/design_calc.htm.

excellent low-temperature performance of EDLCs is also a critical advantage for many applications.

Electric double-layer capacitor technology is now sufficiently proven that EDLCs are deployed in a wide range of civilian applications, in all of the form factors shown in Figure 3. For example, small ELDCs are being incorporated into hand-held electronics to supply pulse power needs,[23] while large-scale EDLCs and EDLC modules are being validated and deployed in applications ranging from hybrid–electric vehicles[24,25] to Uninterrupted Power Supply (UPS) systems for backup/bridge power[26] that support local and regional electric power delivery. The fast charge–discharge response (on the order of one second or less) of EDLCs is particularly effective for regenerative energy capture in hybrid–electric systems, but is also beneficial for addressing power quality issues (voltage sags and spikes) in local and regional electricity grids.[27] The principal limitation of EDLCs is their relatively low energy densities. To compensate for this limitation, EDLCs can be paired in parallel with conventional batteries in a hybrid power source, where the EDLC meets momentary power needs and the battery provides long-term power. Using the EDLC to bear the burden of pulse power demands often extends the operational lifetime of the associated battery.

Asymmetric ECs with Aqueous Electrolytes. Although EDLCs exhibit many desirable properties with respect to durability and fast charge–discharge response, their energy density is fundamentally restricted by their reliance on double-layer capacitance (a surface-limited process) as the primary charge-storage mechanism. In an effort to address this limitation, another class of ECs has been developed in

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23. See http://www.cap-xx.com/resources/app_briefs/app_briefs.htm.
24. See http://www.nesscap.com/data_nesscap/A.Burke.pdf.
25. See http://www.maxwell.com/pdf/uc/white-papers/200904_WhitePaper_AutomotiveElectronics_ASchneuwly.pdf.
26. See http://www.maxwell.com/pdf/uc/white-papers/200904_WhitePaper_EDNEurope_ASchneuwly.pdf.
27. See http://www.maxwell.com/pdf/uc/white-papers/200904_WhitePaper_VoltageSags.pdf.

which two distinct electrodes are used in an asymmetric configuration: (*i*) a high-surface-area carbon electrode, in which charge storage is based on double-layer capacitance, and (*ii*) a "battery-type" opposing electrode (typically a metal oxide) that relies on faradaic mechanisms for charge storage.[28] By carefully pairing the two types of electrode materials one can achieve devices that exhibit much higher energy densities than EDLCs, while maintaining a relatively fast charge–discharge response when compared to conventional batteries. The use of a faradaic material with a fixed thermodynamic potential may also lessen self-discharge in asymmetric ECs relative to their EDLC counterparts.

The most common asymmetric capacitor configurations use a faradaic metal oxide cathode (positive electrode), such as PbO_2 or NiOOH, and an activated carbon double-layer anode (negative electrode) in conjunction with a concentrated aqueous electrolyte (H_2SO_4 or KOH). Because of the high overpotential of the carbon anode for the hydrogen-evolution reaction, cell voltages of 1.5–2.2 V can be achieved with such asymmetric cell configurations, far beyond the thermodynamic voltage window for aqueous electrolytes (~1.2 V). This extension of the operating voltage range mitigates the one disadvantage of aqueous electrolytes, which otherwise are preferred to nonaqueous electrolytes due to their low cost, high ionic conductivity, high electrolyte solubility, and less rigorous cell-packaging requirements. The use of aqueous electrolytes also provides an advantage in terms of safety when compared to energy-storage technologies (*e.g.*, EDLCs and Li-ion batteries) that incorporate volatile, flammable organic solvents. Due to the combination of large operating voltages for the asymmetric cell design and the faradaic capacity of the metal oxide positive

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28. W.G. Pell and B.E. Conway, "Peculiarities and Requirements of Asymmetric Capacitor Devices Based on Combination of Capacitor and Battery-Type Electrodes," *J. Power Sources* **136**, 334 (2004).

electrode, relatively high energy densities can be achieved. For example, Zheng reported the maximum theoretical energy density of a NiOOH‖carbon asymmetric capacitor as 40 W h kg^{-1},[29] an energy density that cannot be achieved with any present or foreseeable EDLC design.

Two general types of asymmetric aqueous ECs are commercially available: (*i*) NiOOH‖carbon cells that use concentrated alkaline electrolytes, and are produced by ESMA[30] in Russia (see Figure 5); and (*ii*) PbO_2‖carbon cells that use sulfuric acid electrolyte, produced by Axion Power International (New Castle, PA).[31] In both cases, these asymmetric ECs are fabricated with internal electrode architectures that are more characteristic of conventional batteries, in that the individual electrodes are thicker than those found in EDLCs. Thus the currently available asymmetric aqueous ECs are not necessarily designed to exhibit the few-second time response of EDLCs, but are rather typically configured for charge–discharge times on the order of a few minutes. However, compared to conventional batteries, asymmetric ECs deliver significantly higher power density, enabled by the capacitive charge-storage processes in the carbon anode.

The NiOOH‖carbon asymmetric ECs from ESMA[30] are available in single cells, with capacitances ranging from 3 to 80 kF and operating voltages of up to 1.7 V, and in multi-cell modules with operating voltages up to 48 V. The typical specific energy densities of single-cell capacitors are ~8–10 W h kg^{-1} which exceeds the typical energy densities of EDLCs (3–5 W h kg^{-1}), while volumetric energy densities for single-cell NiOOH‖carbon asymmetric ECs are on the order of 12–15 W h L^{-1}. The maximum specific power for ESMA ECs are as high as 3 kW kg^{-1}

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29. J. P. Zheng, "The Limitations of Energy Density of Battery/Double-Layer Capacitor Asymmetric Cells," *J. Electrochem. Soc.* **150**, A484 (2003).
30. See http://www.esma-cap.com/?lang=English.
31. See http://www.axionpower.com.

with a charge time of <15 minutes. The recommended operating temperatures for ESMA ECs are between –50 and +50 °C, primarily dictated by the properties of the KOH electrolyte. The cycling stability of ESMA NiOOH‖carbon ECs has been demonstrated from tens-to-hundreds of thousands of cycles, compared to conventional batteries whose typical cycle life is a few thousand cycles. Self-discharge in the ESMA ECs is also slow, and they can retain their charge for a period of several months.

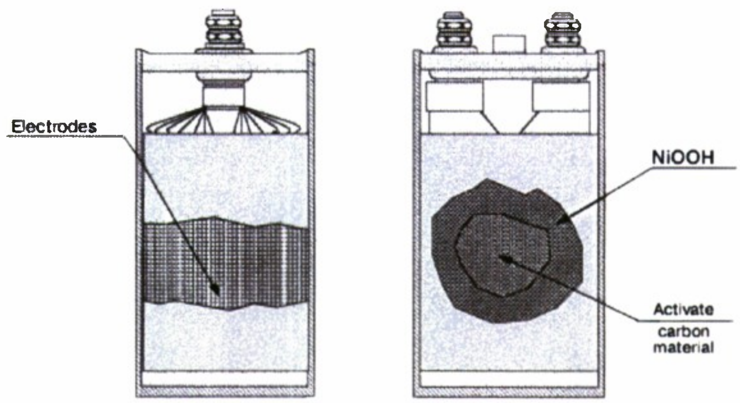

Figure 5. Schematic of ESMA NiOOH‖carbon EC (see reference 29).

The NiOOH‖carbon asymmetric ECs are presently being deployed in a number of mobile[32] and stationary[33] applications. Their most visible use has been in hybrid-electric buses that operate in Moscow. The ESMA ECs are also being investigated as energy-storage solutions for small industrial equipment, such as forklifts, to replace the batteries that are currently used. Although ESMA ECs have lower energy densities than conventional batteries, their rapid-recharge capabilities can be exploited when a central power system is available to recharge them at regular intervals, resulting in overall operational time that is greater than obtained with battery-based energy storage.[34] For stationary uses, ESMA is designing uninterruptible power systems (UPS) that incorporate its asymmetric ECs in order to address power quality problems that are encountered in

32. See http://www.esma-cap.com/Use/Transportation/@lang=English
33. See http://www.esma-cap.com/Use/Stationary/@lang=English
34. See http://www.esma-cap.com/FAQ/doc1eng@lang=English

applications ranging from computer systems to large-scale industrial manufacturing. New EC modules being developed by ESMA are designed with power and energy density characteristics that allow them to bridge power interruptions that typically last a few seconds, mitigating potential failures in the complex systems that are being powered.

The second common design for asymmetric aqueous ECs is based on the PbO_2 ǁ carbon configuration, which uses a sulfuric acid electrolyte. This cell design is closely related to a lead-acid battery, except that the normal Pb anode is replaced with a high-surface-area capacitive carbon anode, while the PbO_2 cathode is retained, storing charge via faradaic processes.

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \leftrightarrows PbSO_4 + 2H_2O$$

The main supplier of such ECs, Axion Power International,[31] actually markets their product as a "PbC® battery", and produces them in form factors (*e.g.*, 12-V modules) that mimic traditional Pb-acid batteries. In terms of both manufacture and usage, the PbC battery modules of the type developed by Axion may serve as a ready high-power replacement for Pb-acid batteries, which are still prevalent in the commercial sector, but also heavily used by the Navy for bulk energy storage. In 2008, Axion Power was awarded a $1.2 million federal grant to develop its PbC® battery technology for use in advanced vehicles for the U.S. Marine Corps.[35]

The energy density for Axion's asymmetric PbC battery is 25 W h kg^{-1}, compared to the ~8–10 W h kg^{-1} for ESMA's NiOOH ǁ carbon ECs, with the higher energy density of the former arising from the higher operating voltage (2.0 V) of the PbC/acid electrolyte cell chemistry. At the time of this writing, detailed specifications for power density and cycle life for the PbC battery system are not

35. See http://www.axionpower.com/profiles/investor/ResLibraryView.asp?BzID=1933&ResLibraryID=27617&Category=1562.

readily available. Axion is targeting their PbC® products for applications ranging from hybrid–electric vehicles and high-performance marine uses to standby power in UPS systems and stationary grid applications (see Figure 6). Both the Axion PbC® and ESMA NiOOH‖carbon asymmetric EC technologies are promising replacements for conventional batteries in support of UPS and grid systems.[33,36] Although conventional batteries provide significantly higher energy densities than the asymmetric ECs, much of that energy density is not tapped when providing power conditioning, peak-shaving, and pulse power capabilities. To achieve the necessary power density for such uses, the battery module must often be over-sized in terms of energy density. The replacement of batteries with either of the asymmetric EC technologies should result in significant reductions in weight and volume necessary for the energy-storage system, while also providing longer cycle life and lower maintenance.

Figure 6. Axion "Power Cube®", a mobile energy storage system that can be configured to deliver up to 1 MW of power for 30 minutes or 100 kW of power for 10 hours (see reference 35).

FUTURE OPPORTUNITIES FOR ELECTROCHEMICAL CAPACITOR DEPLOYMENT IN NAVY/MARINE CORPS MISSIONS

Hybrid–Electric Vehicles for Land-Based Operations. The application of hybrid–electric power systems for light-duty vehicles (compact cars to pickup trucks and sports-utility vehicles) is now commonplace, with many models available on the market. Less visible, but no less important, are heavy-duty vehicle platforms (*e.g.*, city buses and garbage trucks) that also benefit from hybrid–electric drive trains.

36. See http://www.axionpower.com/profiles/investor/fullpage.asp?f=1&BzID=1933&to=cp&Nav=0&LangID=1&s=0&ID=10303.

These vehicles are available with a variety of hybrid–electric designs, ranging from "micro" or "mild" hybrids that serve in a "stop/start" function to minimize idling of the combustion engine, to "full" hybrids in which the vehicle can operate in an all-electric mode for short distances at low speeds. Energy storage is a key component of any hybrid–electric system, being used to both harvest energy through regenerative braking and to deliver that energy for quick bursts of acceleration or low-speed operation, reducing the power demands on the vehicle's combustion engine. Batteries are presently the most common form of energy storage used in commercially available hybrid–electric vehicles, but the rapid charge–discharge capabilities and long cycle life of ECs are now drawing attention to their use for hybrid–electric platforms.

The U.S. military has recognized the potential benefits of hybrid–electric vehicle platforms in terms of reduced fuel consumption, promising not only monetary savings, but also reduced risks to personnel associated with fuel transport through hostile environments, such as those recently seen in operations in the Iraqi theater.[37] The adaptation of hybrid–electric systems to military transportation platforms has proceeded at a much slower pace than for the commercial sector, due in part to the increased complexity, lower production volumes, and demanding requirements of military hardware. However, there are a few development programs currently underway. The U.S. Army is the obvious leader in such efforts, but as in many other cases, new land-based technologies developed for the Army are often applicable and adaptable to Marine Corps missions.

37. L.P.Farrell, Jr., "Alternative Energy Needed for More than Just Cost Savings," *National Defense Magazine*, December 2008 (see http://www.nationaldefensemagazine.org).

A prime example is the "Heavy Expanded Mobility Tactical Truck" (HEMTT) produced by Oshkosh Truck Corporation, a vehicle with a proven track record as a transport for supporting combat units and weapons systems. Over the past few years, Oshkosh has developed the ProPulse™ diesel–electric series hybrid system that is incorporated into the "A3" version of the HEMTT.[38,39] The ProPulse™ system is designed such that the diesel engine, operating at constant speed, drives a generator that in turn powers electric motors at each differential. Energy storage for the ProPulse™ system is provided exclusively by a 1.9-MJ bank of Maxwell BOOSTCAP® EC modules, with no additional batteries required. The EC bank captures energy dissipated during braking, and provides short-term bursts of power to the electric drive motors when acceleration is needed, allowing the diesel engine to remain operating in a high-efficiency mode. By redesigning the HEMTT with a hybrid–electric drive, fuel economy is increased by ~20% relative to the non-hybrid equivalent. The initial version of the HEMTT-A3 will be produced for the Army, with a similar version to follow that will be designed to Marine Corps specifications.

Figure 7. Oshkosh Truck HEMTT-A3 with ProPulse™ hybrid–electric drive.

The benefits of redesigning military vehicles with hybrid–electric drive systems extend beyond gains in fuel efficiency. Hybrid–electric vehicles, particularly those with serial hybrid designs, can also serve as mobile power-

38. See http://oshkoshdefense.com/defense/products~a3~home.cfm.
39. T. Lataik, "The Army Goes Green," *Popular Mechanics*, April 22, 2006.

generating stations, fulfilling the military's vision for "islands of power" in the field.[40,41] For example, the Oshkosh HEMTT-A3 can provide 100 kW of exportable, military-grade AC power from its hybrid–electric system. Integrating such power-generation capability into the vehicle platform may ultimately reduce the need for separate tow-behind generator sets ("gensets"). While awaiting the further evolution and deployment of hybrid–electric military vehicle platforms, the hybrid concept can also be applied to gensets themselves, where energy-storage based on ECs can be used to address intermittent pulse-power demands, leaving the diesel engine of the generator to operate at its most efficient speeds, resulting in lower fuel consumption.[42]

For the foreseeable future, diesel engines will be the preferred energy conversion technology for both transportation and portable power generation, but in the longer term, fuel cells may ultimately gain acceptance for these same tasks. The benefits of the hybrid–electric concept can also be realized for fuel cells by pairing them with energy storage, such that the fuel cell can operate at constant power conditions for maximum efficient, while the energy-storage unit is used for momentary pulse-power. Although both batteries and ECs have been demonstrated in hybrid configurations with fuel cells, ECs appear to be more promising for this application.[43]

Sea-Based Cargo-Transfer Cranes with Integrated Hybrid–Electric Power Systems. Moving into the 21st century, the U.S. Navy developed "Sea Power 21" as the guiding vision for future Navy/Marine Corps operations, which will

40. "Hybrid Electric Vehicles: Battlefield 'Islands of Power?'" *National Defense Magazine*, September 2006 (see http://www.nationaldefensemagazine.org).
41. C. Lowe, "Hybrids Got the Juice," http://www.defensetech.org/archives/002338.html.
42. M. J. Ampela, "Advanced Hybrid Electric Diesel Generator Sets Based on Carbon Foam Ultracapacitors," *Proceedings of the 43rd Annual Power Sources Conference*, Philadelphia, PA, July 2008.
43. W. Gao, "Performance Comparison of a Fuel Cell-Battery Hybrid Powertrain and a Fuel Cell-Ultracapacitor Hybrid Powertrain," *IEEE Transactions on Vehicular Technologies* **54**, 846 (2005).

integrate information superiority and dispersed, networked force capabilities to address security issues around the globe.[44] A key component of the Sea Power 21 vision is the "Sea Basing" concept, which exploits the expanse of the sea as a foundation from which air, sea, and land capabilities can be projected and supported, lessening the reliance on land bases in hostile areas. The success of the Sea Basing concept relies in part on technologies that enable efficient and rapid transfer of supplies and equipment from ship-to-ship and ship-to-shore. The High Capacity Alongside Sea Base Sustainment (HiCASS) project (see Figure 8) supports this mission through the development of ship-to-ship cargo transfers via special ship-board crane systems that are designed to operate under a wide variety of sea states.[45,46]

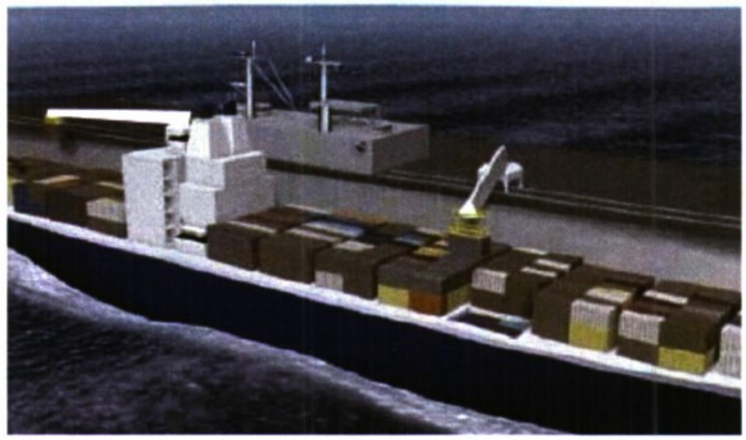

Figure 8. Illustration of HiCASS concept.(see reference 46).

Oceaneering Technologies[47] is presently conducting research and development in support of the HiCASS program, one aspect of which involves the addition of an EC-based energy-storage system ("Regenerative Ship Motion Induced Energy Storage") to augment the operation of shipboard cranes in a hybrid–electric configuration. Hybrid–electric transfer cranes are not a new concept, and in fact are now being gradually adopted in busy seaports

44. See http://www.navy.mil/navydata/cno/proceedings.html.
45. See http://www.globalsecurity.org/military/systems/ship/systems/hicass-lvi-lolo.htm.
46. See http://www.oceaneering.com/brochures/Pdfs/hicass.pdf.
47. See http://www.oceaneering.com/otech.asp?id=1080&fragment=0&SearchType=AND&terms=hicass.

worldwide.[48] The repetitive "lift–lower" motion of cranes used to transfer cargo between ship and shore is ideal for operation with a hybrid–electric system, in which a significant fraction of the energy expended in the lift cycle can be recaptured during the lower cycle and then delivered again during the lift cycle to augment the power from the main power source (typically a diesel engine). The result is an overall decrease in fuel consumption and associated air pollution with the hybrid–electric crane system compared to a conventional crane.

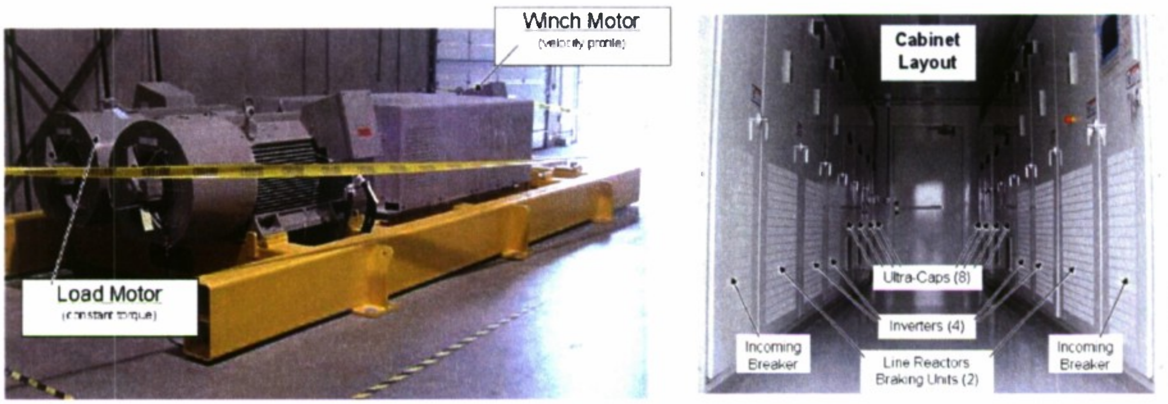

Figure 9. HiCASS D2 Test Motor Stand (left) and (right) HiCASS D2 Energy Storage Process Control Room Interior.

The power requirements of ship-based cranes that are being developed in the HiCASS program may significantly strain the generating capacity of many current naval vessels. By reconfiguring these systems in hybrid–electric configurations with appropriate energy storage technology, the power demands for crane operation may be significantly reduced, as is the case with the seaport cranes described above. However, the HiCASS systems may have more demanding requirements than already proven land-based cranes, including higher duty cycles and higher cycle periods (7–8 seconds). To examine the feasibility of the hybrid–electric concept for HiCASS crane applications, Oceaneering

48. See http://www.greencarcongress.com/2006/08/hybridelectric_.html)

Technologies is performing proof-of-principle experiments using a test rig (see Figure 9) composed of an electric hoist system that is interfaced with an energy storage system that is composed of four banks of Maxwell BOOSTCAP® EC modules, each providing 2 MJ of storage capacity at full charge.[49]

Early results from the prototype system developed and tested by Oceaneering clearly demonstrate the advantages of mating EC-based energy storage with the electric hoist rig.[50] For example, Figure 10 shows the power flow for a typical lift–lower cycle, where the "Rect_Pwr" curve represents external power applied to the system (a stand-in for the power that would be applied to the electric hoist from the ship's generation system), and "Bus_Pwr" curve represents the charging of the EC module bank on the lower segment and subsequent power delivery to the hoist on the lift segment of the cycle. As seen from these results, the external power needed in the lift segment is substantially lower than that supplied by the capacitor bank; in this specific test the contribution of the "ship power" during the complete lift–lower cycle represents only 11% of the total energy consumption.

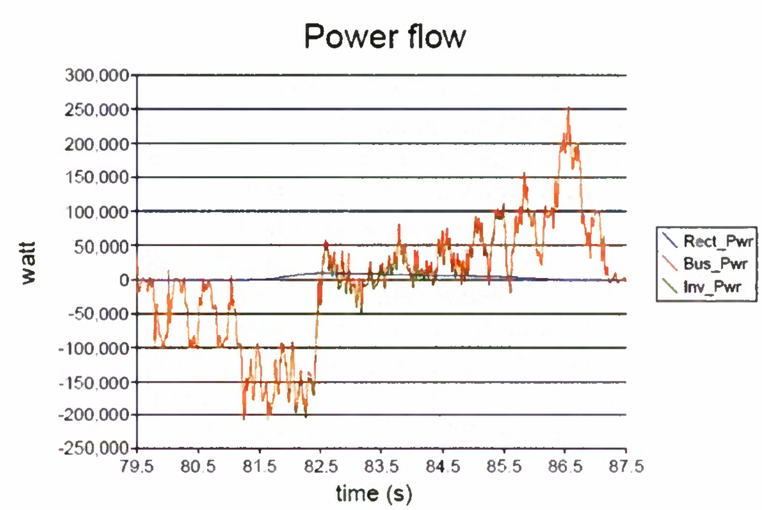

Figure 10. Typical cycle test for HiCASS D2 system, showing power flow for the externally applied power ("Rect_Pwr) and the power to/from the energy-storage unit ("Bus_Pwr").

49. Technical information on the HiCASS Technology Demonstration D2 Energy Storage project provided by Ed May of Oceaneering International, in conjunction with program manager, Dr. Paul Hess of the Office of Naval Research (Code 331).

50. W. Thompson and R. Adams (Oceaneering International), "HiCASS Technology Demonstration D2 Energy Storage Final Report," *Document #HiC-T-00400*, 12 September 2007.

In addition to providing regenerative energy capture and delivery during normal operations, the EC energy-storage system can also provide emergency payload recovery in the event of a loss of the main power supply. In a "loss of ship power" test with this same prototype system, the hoist continued to operate for five additional lift cycles after the external power supply was disconnected (simulating loss of ship power), with power supplied from the energy-storage bank until a cut-off bus voltage was reached (see Figure 11).

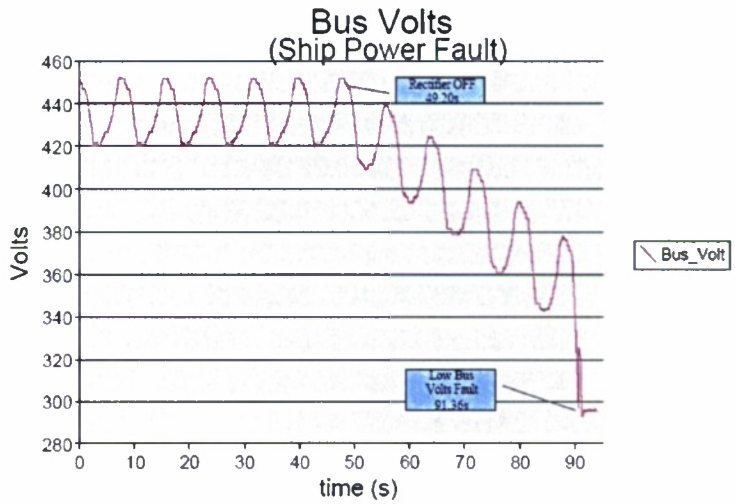

Figure 11. "Loss of ship power" test for HiCASS D2 system, showing the bus voltage during a series of lift-lower cycles. External power is disconnected at t = 49.2 s, after which the hoist continues its lift–lower function for five additional cycles, powered only by the energy-storage unit.

The HiCASS D2 system clearly demonstrates the advantages of EC-based energy storage (in this case with EDLCs) for applications with demanding duty cycles and repetitive motion, particularly with respect to reducing the power demands on the primary generation source. The end result is lower fuel consumption and associated extended operating range, lower emissions, and potentially greater design flexibility with respect to the power-generation architectures of future naval vessels. Future development of related designs that incorporate EC-based energy storage would be beneficial for other shipboard systems, such as personnel transfer, launch and recovery, and motion compensating ramps and platforms.[49,50]

Electrochemical Capacitors as an Enabling Energy-Storage Technology in Support of Advanced Power Architectures for Naval Vessels. Electrochemical energy-storage systems have been an integral component of naval designs since the time of Edison,[51] most prominently used in diesel submarines as power sources during sub-surface operations. Over the intervening century, electrochemical energy storage, most commonly in the form of batteries, has been incorporated into many sub-systems of ships and submarines, providing backup power to both centralized and distributed operations. As naval vessels continue their evolution into the 21st century with new platforms such as the "CG(X)" cruiser (Figure 12) and their associated advanced offensive and defensive weapons systems,[52] the requirements for shipboard power architectures are growing increasingly complex and demanding. To meet this challenge, concepts such as "Integrated Power Systems"(IPS)[53] are being developed, with the goal of greater integration of power generation, distribution, and consumption systems to ultimately enhance warfighting capabilities, and reduce unnecessary redundancy and complexity. Energy storage will remain a key component for these advanced ship designs, and with the relatively recent emergence of ECs as a viable and proven alternative to batteries for certain functions, the incorporation

Figure 12. Artist conception of CG(X) Cruiser

51. "Edison Lessens Submarine Peril," *New York Times*, 18 April 1915.
52. See http://www.navy.com/about/shipsequipment/navyofthefuture/cgx/.
53. Capt. N. Doerry, "Next Generation Integrated Power Systems (NGIPS) for the Future Fleet," *IEEE Electric Ship Technologies Symposium*, Baltimore, MD, 21 April 2009. See http://ewh.ieee.org/conf/ests09/ESTS-2009%20Capt%20Doerry.pdf

of ECs into these new shipboard power distribution architectures should be strongly considered.

While the specific types and functions of energy storage in many of these new power architectures have yet to be determined, one can draw informative comparisons with the present and planned deployment of EC-based energy storage for electric power management in the commercial sector, in particular by electric utilities and telecom companies. The power architecture of naval vessels, particularly those with advanced electric designs such as the IPS, have much in common with a land-based electricity grid—centralized power generation feeding a distribution network with associated power-management electronics and hardware working together to meet the diverse and ever-changing power requirements of its "customers." Likewise the power architecture of a naval vessel must be designed to support many and varied functions, including propulsion, radar, communications, cargo and personnel transfer, advanced weapons systems, and defensive capabilities, each of which have distinct power requirements.

Electrochemical capacitors are gradually being adapted as components of power delivery systems, in uses ranging from small UPS systems that power local computer networks, to on-site power delivery systems for manufacturing facilities, and in support of power distribution in larger electrical grid systems. In all cases, electrochemical capacitors are used to improve the quality, continuity, and reliability of electric power distribution, which can be plagued by interruptions, and voltage sags and spikes on the order of milliseconds to several minutes. These interruptions can cause critical and costly equipment failures, downtime, and increased operational costs in civilian applications, but when these same power-quality issues are encountered within the power architectures of naval vessels, their operational capabilities may be seriously compromised.

Modern electronics are particularly vulnerable to voltage sags and spikes (often only milliseconds in duration), which can seriously impair their operation. These short-term disruptions may arise from the power-generation source or more frequently on the consumption side for systems with many components that have varying and intermittent power requirements. The fast charge–discharge response of EDLCs can be exploited to mitigate the effects of such voltage interruptions.[54,55] Because the carbon electrodes in EDLCs do not have a well-defined thermodynamic potential, the EDLC itself has "flexible" voltage characteristics, which allows it to more easily address momentary voltage sags that propagate through the associated power bus. This "hardening" of the power distribution system requires only a few EDLCs distributed at key points near the power bus.

Electrochemical capacitors are also used as energy storage in UPS systems for bridge-power/backup-power functions to address longer-term disruptions in the main power supply. These power disruptions are typically on the order of a few seconds to several minutes, and are encountered when switching between primary generation sources (planned or unplanned). Because most power-generation systems do not start-up instantaneously, UPS are designed to provide the "bridge" power until the principal power supply is restored. Electrochemical capacitors are gradually replacing conventional batteries in some UPS systems due to their demonstrated power density advantage and long lifetime.[56] The lower energy densities of ECs are not a particular hindrance in this application, as most UPS systems are required to supply power for only a few minutes. However, the higher densities of asymmetric aqueous ECs (NiOOH‖carbon or

54. B.M. Han and B. Bae, "Unified Power Quality Conditioner with Super-Capacitor for Energy Storage," *Euro. Trans. Electr. Power* **18**, 327 (2008).
55. See http://www.maxwell.com/pdf/uc/white-papers/200904_WhitePaper_VoltageSags.pdf.
56. See http://www.maxwell.com/pdf/uc/white-papers/200904_WhitePaper_BridgePower.pdf.

PbO_2‖carbon) relative to EDLCs may make the asymmetric aqueous EC the more attractive choice for UPS systems (see Figure 13).[57]

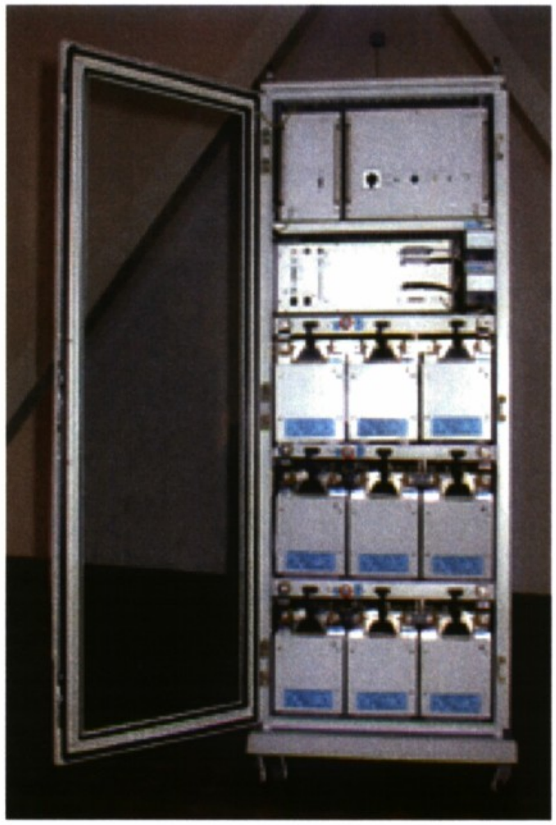

Figure 13. A 100-kW UPS (Ride-Through) system developed by ESMA, using of nine "30EC402 U" modules connected in series, as an energy storage device. This system has 600-V DC operating voltage and support time of not less than 10 seconds at 100-kW discharge power.

On a typical naval vessel, dozens of UPS systems are dispersed throughout the ship, with each individual system requiring its own energy-storage module, which is most commonly a bank of conventional Pb-acid batteries. Because Pb-acid batteries are not designed for high-power functionality, the battery bank must be significantly oversized to meet the power-density requirements of the UPS system. Replacing the traditional Pb-acid battery bank with ECs, most likely in the form of NiOOH‖carbon or PbO_2‖carbon asymmetric ECs, should reduce the mass and volume footprints of the energy-storage module and provide extended operation lifetime and lower maintenance costs.

As naval ship design evolves toward integrated power architectures, advanced power-generation systems, such as solid-oxide fuel cells will become more prominent components. As described in the previous sections on

57. See http://www.esma-cap.com/Use/Stationary/@lang=English#N120AA6.

transportation, coupling EC-based energy storage with a fuel cell can result in significant gains in performance and efficiency, allowing the fuel cell to operate in its most efficient constant-power mode while the ECs are used to meet momentary pulse-power demands. These same benefits would apply to ship-board fuel cell systems.

Application of Electrochemical Capacitors for Mobile Electronics and Communications. The useful forms of ECs are not limited to the large cells or multi-cell modules described above for transportation or utility applications. Small EDLCs with capacitances on the order of tens of farads are being increasingly utilized in the commercial sector for hand-held electronic devices, including cell phones, cameras, PDAs, and even wireless sensors. For such applications, a small EDLC is typically coupled in parallel with a battery, with the EDLC providing short pulses of power as needed, and the battery recharging the capacitor between pulse demands and meeting longer-term low-power demands. A prime example is powering the LED flash of a cell-phone camera as shown in Figure 14.[58] The same benefits of EDLC incorporation can be realized for wireless

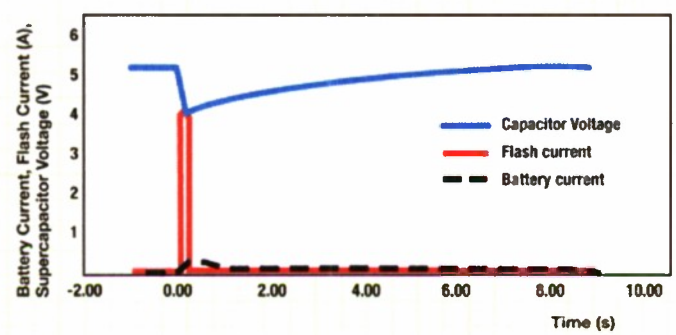

Figure 14. Cell-phone camera flash operation with EC–battery hybrid power source. The EDLC provides 4-A flash current (red) while discharging from 5.2 to 4.0 V, and the battery provides 300-mA charge current (black) to the EDLC.

58. See http://www2.electronicproducts.com/Supercapacitors_for_mobile-phone_power-article-farr_capxx_dec2007-html.aspx.

communications, particularly those that operate with "burst-mode" functions, which require intermittent high-power pulses for signal transmission. The excellent low-temperature performance of EDLCs can also be exploited to offset the relatively poor low-temperature function of conventional batteries when the two are paired together in a hybrid EDLC–battery power source.[59] The benefits of incorporating EDLC-based pulse power capabilities into small electronics will of course have the same and potentially even greater benefits for military versions of these same technologies.

Future Outlook for EC Technology

As outlined in this report, ECs are only beginning to make an impact in the private sector as an energy-storage solution, where even the present level of performance is attractive for many specialized uses. While current-generation ECs find their way into more real-world applications, the evolution of next-generation EC technologies continues at the basic and early applied research levels, through the development of new nanostructured electrode materials and advanced electrolytes,[7,8] the introduction and improvement of new cell configurations and chemistries, and from greater fundamental understanding of the interfacial electrochemical processes that undergird EC operation.

Carbon–carbon EDLCs represent the most advanced EC technology with respect to commercialization, and as such, dominate the small but growing market for ECs. Although a mature technology, the performance of EDLCs may be further improved through continuing research and development efforts. At the materials level, further "engineering" of the pore structures of synthetic carbons should improve their gravimetric and volumetric capacitances,[13] but will likely produce only an incremental increase in the energy densities of EDLCs. Because

59. See http://www.cap-xx.com/resources/app_briefs/ab1012.pdf.

of the square-dependency relationship of the cell voltage to the energy density, extending the operating voltage beyond the current 2.7 V limit with acetonitrile-based electrolytes will have a greater impact on the energy density, which remains a key limitation of EDLC performance. Many alternative "high-voltage" electrolyte systems are under investigation, ranging from ionic liquids to organosilicon-based polymers, but the use of these advanced electrolytes may ultimately involve tradeoffs in terms of lower power and higher cost. However, for specialized uses, for example where operating temperatures exceed 60 °C are required, such electrolytes may prove crucial.

Many EC concepts are moving beyond reliance on double-layer capacitance for charge-storage, incorporating such materials as mixed ion/electron-conducting metal oxides and conducting polymers that store charge by faradaic processes. The asymmetric aqueous EC technologies described in the preceding sections are a prime example. In addition to delivering significantly higher energy densities than EDLCs, the NiOOH‖carbon and PbO_2‖carbon ECs also provide the safety and low-cost benefits that are associated with the use of aqueous electrolytes. The performance and applicability of these EC technologies could be further enhanced through the use of nanostructured electrode materials and more compact electrode designs that would reduce their charge–discharge response times from several minutes to a few seconds, concomitantly increasing their power densities. In the past few years, manganese oxides have attracted much attention as potential lower-cost alternatives to NiOOH and PbO_2 for aqueous asymmetric ECs.[60] Manganese oxide-based ECs are also distinguished by their use of nominally pH-neutral aqueous electrolytes (*e.g.*, Na_2SO_4 or Li_2SO_4) that are less hazardous than the concentrated basic and acidic electrolytes used for

60. T. Brousse, D. Bélanger, and J. W. Long, "Manganese Oxides: Battery Materials Make the Leap to Electrochemical Capacitors," *Interface* **17 (1)**, 49–52 (2008)

NiOOH‖carbon and PbO_2‖carbon ECs, respectively. Progress in the emerging field of MnO_2-based ECs extends from the development of high-performance nanostructured MnO_2 electrode materials,[61] to prototype cell development[62] and early-stage commercialization interest.[63]

The asymmetric design concept has also been extended to cells that incorporate nonaqueous electrolytes, where higher cell voltages (3–4 V) can be achieved.[64] As one example, Amatucci and co-workers have developed asymmetric ECs that use nanostructured $Li_4Ti_5O_{12}$ as a faradaic negative electrode and activated carbon as a combination double-layer/intercalation positive electrode, ultimately yielding ECs with energy densities of 10–15 W h kg^{-1} and power densities of 1000–2000 kW kg^{-1}. This "hybrid supercapacitor" technology (see Figure 15) has been developed in part through support from the Office of Naval Research over the past several years, and as a result is nearing the point of commercialization and potential deployment for military applications.

Figure 15. Photo of a "hybrid supercapacitor" cell prepared at Rutgers University.

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61. A. E. Fischer, K. A. Pettigrew, D. R. Rolison, and J. W. Long, "Incorporation of Homogeneous, Nanoscale MnO_2 within Ultraporous Carbon Structures via Self-Limiting Electroless Deposition: Implications for Electrochemical Capacitors," *Nano Lett.* 7, 281–286 (2007).
62. T. Brousse, P. L. Taberna, O. Crosnier, R. Dugas, P. Guillemet, Y. Scudeller, Y. Zhou, F. Favier, D. Bélanger, P. Simon, "Long-Term Cycling Behavior of Asymmetric Activated Carbon/MnO_2 Aqueous Electrochemical Supercapacitor" *J. Power Sources* **173**, 633 (2007).
63. "Asymmetric Electrochemical Supercapacitor and Method of Manufacture Thereof," S. M. Lipka, J. R. Miller, T. D. Xiao, and D. E. Reisner; U.S. Patent #7,199,997, issued 3 April 2007
64. I. Plitz, A. Dupasquier, F. Badway, J. Gural, N. Pereira, A. Gmitter, and G. G. Amatucci, "The Design of Alternative Nonaqueous High Power Chemistries," *Appl. Phys. A* **82**, 615-626 (2006).

With continued support from the public and private sectors, the present trajectory of EC technology development will ultimately yield energy-storage solutions that enable many applications with challenging energy/power requirements, ranging from small electronics to local electricity grids. The same promising attributes of present and next-generation ECs should also be exploited in support of future Navy and Marine Corps missions.

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